Formation and upper critical fields of the two distinct A15 phases in the subelements of Powder-In-Tube Nb₃Sn wires

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It is well known that the A15 layer in the subelements of a Powder-In-Tube (PIT) Nb₃Sn wire exhibits two different grain morphologies: a region with fine grains (∼200 nm in size) representing about 60% of the total A15 area and one with large grains (1-2 μm in size). By means of high field specific heat and magnetization measurements we have shown that these two A15 phases correspond to two distinctly different T_c distributions, the large grains region exhibiting a higher T_c and a lower B_{c2}, the fine grains region a lower T_c and a higher B_{c2}. We report here the values of the superconducting parameters (T_c, B_{c2}) of the two A15 phases, as determined from an original model to fit the experimental T_c distribution. After a prolonged reaction treatment (625°C/320h), an increase of the fine grain region was observed at the expenses of the large grain region, the B_{c2}(0K) value of the former being raised from 28.8 to 31.7 T. These changes explain the marked increase of J_c to 2'700 A/cm² at 4.2K/12T, the highest value measured so far in PIT wires.

High performance Powder-In-Tube (PIT) Nb₃Sn wires are currently being developed and tested for the next generation of accelerator magnets, in particular for the Large Hadron Collider (LHC) upgrade with high luminosity at CERN. In recent years there has been a remarkable increase of the critical current density J_c at the operating temperature and magnetic field. After optimization of the reaction schedule the PIT conductor developed in the frame of the EU-supported Next European Dipole (NED) project has achieved a non-Cu J_c value of 2'700 A/mm² at 4.2 K and 12 T[1]. Further improvements require the simultaneous optimization of Sn composition and grain morphology which can be achieved through a deeper understanding of the interplay between reaction conditions and superconducting properties. It is well known that various regions can be distinguished in the subelements of PIT wires after reaction: a layer of large (∼1 μm in size) A15 grains enclosed in a layer of fine (∼200 nm in size) A15 grains, all surrounded by the unreacted Nb or Nb7.5wt.%Ta tube. The reaction process also results in a radial compositional gradient, the average Sn composition being 22 at.% and 24.5 at.% in the fine and large grain regions, respectively[2,3]. However, the precise superconducting parameters for the two regions were not precisely known. In the present work, we have determined the values of the superconducting parameters, the critical temperature T_c and the upper critical field B_{c2}, of the two A15 regions by performing low temperature specific heat measurements. This technique allows the determination of the T_c distribution within the A15 layer[4], ruling out percolation and/or shielding effects generally present in the conventional resistive and magnetic measurements. The examined wire is the PIT conductor B215 manufactured by ShapeMetal Innovation (SMI, now part of Bruker EAS) for the NED project. The conductor has a diameter of 1.25 mm and contains 288
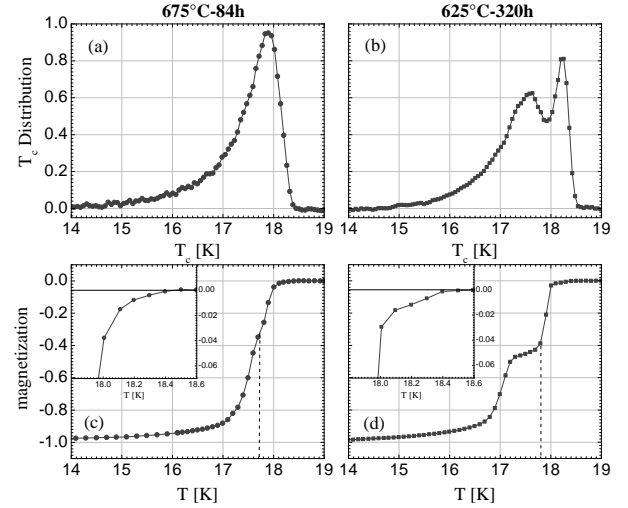

FIG. 1. Distribution of T_c for the PIT wire B215, after reaction at 675°C for 84h (a) and at 625°C for 320h (b). The corresponding magnetization vs. temperature curves are reported in (c) and (d) and magnifications of the transition onset are included as insets. Two peaks are present in the T_c distribution of the wire reacted at 625°C. A double superconducting transition is also present in the M(T) curves.

Nb-7.5wt%Ta tube subelements, whose size is ∼50 μm. The Sn precursor consists of a mixture of NbSn₂ and Sn particles, a Cu layer being interposed between these powders and the surrounding NbTa tube. Two different heat treatments were performed: the SMI-recommended reaction schedule of 84h at 675°C and the optimized reaction schedule of 320h at 625°C that leads to enhancement of J_c(4.2K,12T) up to 2'700 A/mm²[1].

The specific heat of the wires was measured from 2 to 25K at magnetic fields (B) of 0, 0.5, 1, 3, 7 and 14T, using

TABLE I. Summary of the physical properties of the two A15 phases

	675°C/84h		625°C/320h	
	Large grains	Fine grains	Large grains	Fine grains
$<T_c>$ [K]	18.2	18.0	18.35	17.83
α	5	9	7	6
σ	0.4	0.9	0.3	0.83
$|dB_{c2}/dT|_{T_c}$ [T K^{-1}]	1.96	2.35	2.04	2.58
B_{c2}(T=0K) [T]	24.6	28.8	25.7	31.7

a long relaxation technique. The distribution of T_c inside the filaments was determined on the superconducting transition, which was isolated from the background of phonons and normal state electrons following the procedure described in Ref.[4]. As a consequence of the Sn composition gradient present in the filaments the T_c distribution for Nb_3Sn wires usually extends down to 14K. Moreover, the distribution curve exhibits a negative skew reflecting the shape of the T_c vs. at.% Sn relation. As shown in Ref.[5] and[6], the variation of T_c with Sn content is essentially linear up to 24 at.% and levels off between 24 and 25 at.%. Therefore, the skewness of the T_c distribution becomes more pronounced for average Sn compositions approaching stochiometry. Fig. 1 illustrates the comparison between the T_c distributions for the wire reacted at 675°C for 84h, following the instructions of the manufacturer and at 625°C for 320h, according to the optimized reaction. For both reaction schedules this wire exhibits an onset T_c of 18.4K. In the T_c distribution of the wire reacted at 625°C for 320h two distinct peaks were observed. This can be related to the morphology of the A15 phases. The two different grain morphologies are the consequence of the complex A15 formation process. As reaction heat treatment starts, several Cu-Sn intermetallic phases are formed from precursors and $NbSn_2$ powders dissolution is almost complete below 440°C[7]. At about 550°C, the first reaction occurring in the Nb tubes is the reformation of $NbSn_2$[7]. Subsequently Sn leaves $NbSn_2$ and Nb_6Sn_5 large grains grow inwards the Nb tube. A first A15 phase is formed on the outside of the Nb_6Sn_5 layer, mainly due to the Sn diffusion from the core. As the reaction proceeds, the Nb_6Sn_5 phase is converted into Nb_3Sn, too. However the grains of this second Nb_3Sn phase retain the size of the Nb_6Sn_5 grains, which is significantly larger than that of the first A15 layer directly formed from the solid state diffusion of Sn into Nb. The two peaks in the T_c distribution thus reflect the relative volume of the large and fine grain regions. As T_c depends on the Sn content, the peak with maximum at 18.2K corresponds to the large grains, whose composition is close to the stoichiometry(average 24.5 at% Sn) as revealed from the Energy Dispersive X-ray Spectroscopy (EDS) analysis reported in Ref.[2]. The T_c distribution with a maximum at 17.6K is correlated to the fine grains, whose average content is ~22 at.%[2]. The presence of a bimodal T_c distribution was recently ob-
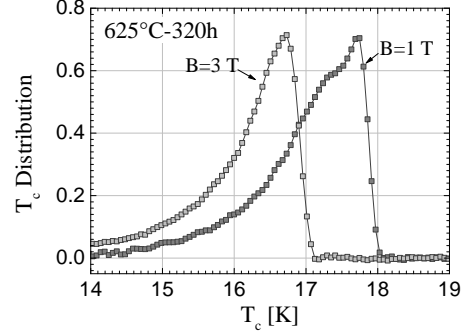

FIG. 2. T_c distribution at B = 1T and B = 3T for the wire reacted at 625°C for 320h. The two peaks tend to merge as the magnetic field is increased.
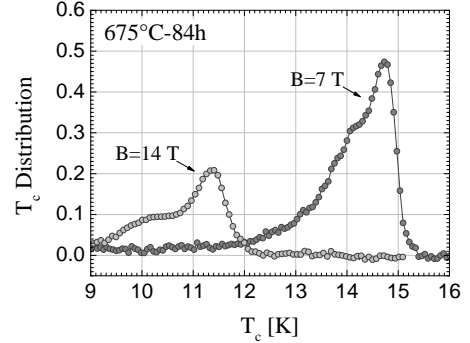

FIG. 3. T_c distribution at B = 7T and B = 14T for the wire reacted at 675°C for 84h. The contribution of large grains appears as a shoulder below the peak temperature.

served in Nb_3Sn bulk samples prepared with the addition of Cu[10]. From the comparison with the results obtained on binary Nb_3Sn samples, the authors conclude that Cu addition triggers the formation of the off-stoichiometric A15 phase responsible for the low-T_c peak in the T_c distribution. In the present work, the superconducting transition was also characterized using a SQUID magnetometer. The magnetization vs. temperature curve, measured at 1 mT and reported in Fig. 1d, also shows two superconducting transitions, thus confirming the specific heat measurements. The lower T_c transition is detected because the higher T_c part is on the inside of the filament, and thus there are no shielding effects. This information
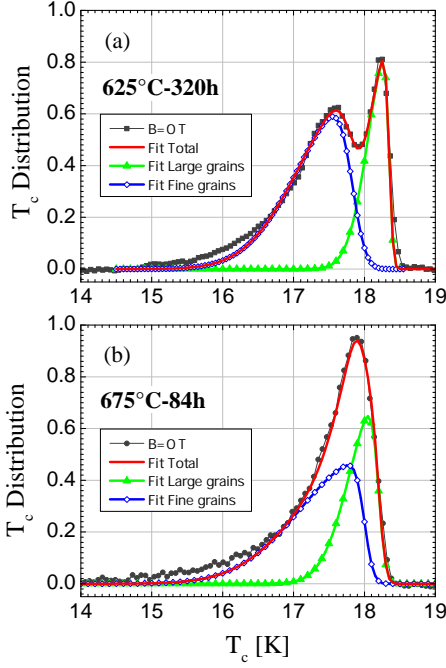
FIG. 4. Fit of the T_c distribution at B = 0T for the wires reacted at 625°C for 320h (a) and 675°C for 84h (b). The contributions from large grains (solid triangles) and fine grains (open diamonds) are reported.

FIG. 5. Fit of the T_c distribution measured in the presence of a magnetic field: B = 1T for the wire reacted at 625°C for 320h (a) and B = 14T for the wire reacted at 675°C for 84h (b). The contributions from large grains (solid triangles) and fine grains (open diamonds) are reported.

about the spatial variation of T_c confirms the identification of the two peaks in the T_c distribution with the two observed grain regions. We also observe the contributions from the two grain families in the inductive T_c measurement performed on the PIT wire reacted at 675°C for 84h (Fig. 1c). However, the onset T_c from the T_c distribution is higher by ∼0.1K compared to the value determined from magnetization , due to the higher sensitivity of the calorimetric technique. In fact, calorimetry detects the thermodynamic transition, whereas magnetometry reveals the presence of screening currents.

As an increasing magnetic field is applied, the two peaks in the T_c distribution of the wire reacted at 625°C for 320h shift towards lower temperatures, but at different rates (Fig. 2), reflecting the different B_{c2} of the two grain families. In particular, we deduce that large grains have lower B_{c2} values. In fact, the field induced shift of the peak corresponding to large grains is more pronounced compared to the behaviour of the peak associated to fine grains. As a consequence the two peaks tend to merge for increasing magnetic fields, as shown in Fig. 2. At B = 3T the T_c distribution exhibits a single peak. The reduced B_{c2} in the large grain region is a consequence of the higher average Sn content: this leads to a higher atomic ordering and, thus, to a lower normal state resistivity[5]. For the wire reacted at 675°C for 84h, it is not possible to discern the two contributions in the T_c distribution at B = 0T, thus indicating a large overlap between the Sn composition ranges of the two
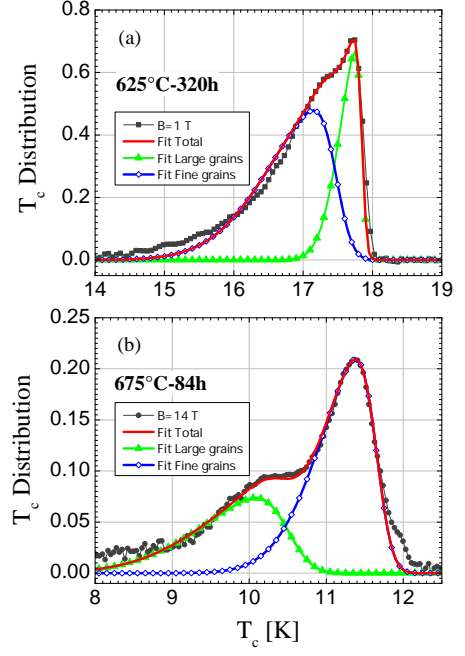
grain families. However, a difference in the B_{c2} values is still present, even if less pronounced compared to the wire reacted at 625°C. As the applied magnetic field is large enough, the contribution to the T_c distribution of large grains, which have a lower B_{c2}, appears as a shoulder in the curve at low temperature. This is shown in Fig. 3 for B = 7T and 14T. The T_c distribution for these PIT wires is thus the superposition of two distribution curves resulting from the two distinct A15 regions. In order to determine the average values of T_c and B_{c2} for fine and large grains, we developed a model to fit the T_c distribution at various magnetic fields. We describe the contribution of each A15 phase as an independent skew normal distribution. The skew normal distribution is a probability function that generalizes the Gaussian distribution to account for the skewness arising from the non-linearity in the T_c vs. at.% Sn relation. It is defined by three parameters: the expected value for T_c, $< T_c >$, the variance σ, reflecting the width of the Sn composition gradient, and the skewness α, whose absolute value increases approaching stochiometry in the Sn composition. The probability density function is given by[8]:

$$ f(T) = \frac{2}{\sigma} \phi \left(\frac{T - < T_c >}{\sigma} \right) \Phi \left(\alpha \frac{T - < T_c >}{\sigma} \right). \quad (1) $$

$\phi(x)$ denotes the standard normal distribution

$$ \phi(x) = \frac{1}{\sqrt{2\pi}} e^{-\frac{x^2}{2}} , \quad (2) $$

with the cumulative distribution function given by

$$\Phi(x) = \int_{-\infty}^{x} \phi(t)\,\mathrm{d}t. \tag{3}$$

Fig. 4 shows the fits of the T_c distribution for the wires reacted at 625°C for 320h (a) and at 675°C for 84h (b). We also report in this figure the two contributions to the T_c distribution from large grains (solid triangles) and fine grains (open diamonds). The volume fraction of the A15 layer occupied by each of the two grain families is determined by integrating the corresponding contribution to the T_c distribution over the explored range of temperatures. It follows that after standard reaction fine grains represent ~60% of the A15 in the wire. This value is raised to ~65% in the sample reacted according to the optimized schedule. The ratio of fine grains is consistent with the estimation of Boutboul et al.[1] on the basis of micrographs on fractured samples. Their Scanning Electron Microscope (SEM) examination showed that $\lesssim$70% of the A15 area is composed by fine grains, for both reaction schedules. From the analysis of the fit results, summarized in table I, it follows that the reaction heat treatment at lower temperature for longer duration leads to the increase of $< T_c >$ in the large grain region ($< T_c > = 18.35$K, compared to 18.2K after standard reaction) and to the decrease of $< T_c >$ in the fine grain region ($< T_c > = 17.83$K, compared to 18K after standard reaction). The reaction parameters also have an influence on the skewness: after heat treatment at 625°C for 320h the skewness in the component of the T_c distribution corresponding to the large grains is increased (α=7, compared to α=5 after standard reaction). For fine grains the skewness of the T_c distribution becomes less pronounced (α=6, compared to α=9 after standard reaction). These results reflect the effect of the optimized heat treatment at 625°C on the Sn composition of the two A15 regions. In particular we argue that in the large grain region the average Sn content is increased while it is decreased in the fine grain region. On the other hand, we observe that the σ values of both large and fine grains do not depend significantly on the heat treatment parameters. This implies that reaction conditions have an influence on the average Sn content in each of the two grain regions but not on the width of the Sn composition gradient. Information regarding the upper critical field B_{c2} of the two A15 regions were obtained extending the fit analysis to the T_c distribution measured in the presence of an external magnetic field. Fig. 5 shows two examples of fitting: the T_c distribution at B = 1T for the wire reacted at 625°C for 320h (a) and at B = 14T for the wire reacted at 675°C for 84h (b). We were able to determine the $< T_c >$(B) - or, equivalently, B_{c2}(T) - dependence for both the A15 regions in a wide range of magnetic fields (Fig. 6). The B_{c2}(0K) values were determined from the data up to 7T, i.e. in the range where the linear approximation of the B_{c2}(T) dependence holds, based on the standard Werthamer-Helfand-Hohenberg (WHH) fitting
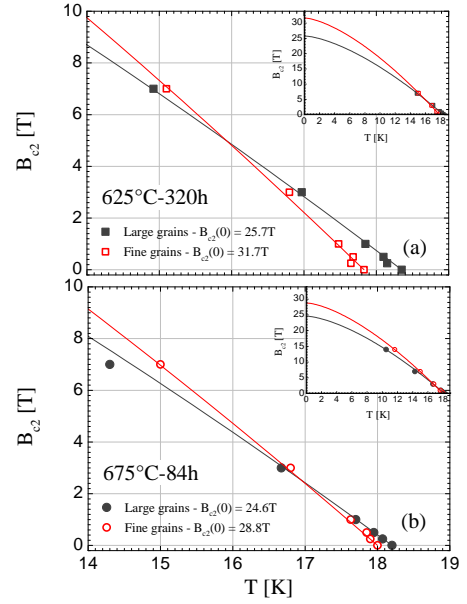

FIG. 6. B_{c2} plot for the two A15 phases, as determined from the fit of the T_c distribution measured at various magnetic fields. (a) Sample reacted at 625°C; (b) sample reacted at 675°C. In the inset the B_{c2} values are extrapolated at T = 0K, following the WHH fitting model. The optimized heat treatment at 625°C leads to a large improvement of B_{c2} in the fine grains.

formula[9]:

$$B_{c2}(0K) = 0.693 < T_c > \left| \frac{\mathrm{d}B_{c2}}{\mathrm{d}T} \right|_{T_c}. \tag{4}$$

Our results are reported in table I, indicating that the optimized heat treatment influences the growth of both large and fine grains, but with a much stronger increase of B_{c2} for the fine grains, where a shift from 28.8T to 31.7T was observed, compared to an improvement for large grains from 24.6T to 25.7T. The extrapolated values of B_{c2}(0K)=31.7T for the fine grain region in the wire reacted at 625°C is rather high. On the other hand, in Ref.[11] Godeke et al. extract from resistivity measurements up to 30T a B_{c2}(0K) of ~29T for a PIT wire reacted at 675°C for 64h, thus in agreement with the value determined by us for the fine grains after standard reaction.

In summary, we have investigated the differences in T_c and B_{c2} for the two A15 phases present in the superconducting layer of PIT Nb$_3$Sn wires by high field calorimetry. After two largely different heat treatments we found in both cases that higher B_{c2} values are achieved in fine grains, in spite of the lower T_c, as a consequence of the enhancement of normal state electrical resistivity for lower average Sn contents. The differences in T_c and B_{c2} between the two A15 phases with different grain sizes are more pronounced for the wire sample reacted at lower temperature for longer duration. The prolonged heat treatment at 625°C facilitates the forma-

tion of an A15 phase with inferior T_c and Sn content but superior B_{c2} at 4.2K. This reflects the influence of reaction kinetics on the atomic ordering and, thus, on the final Sn composition. Since fine grains are directly formed from the Sn diffusion into Nb, while large grains from the Sn depletion of the Nb_6Sn_5 phase, we suggest that the two A15 regions follow different ordering kinetics. In particular, measurements performed on samples reacted for up to 500h show that thermodynamic equilibrium is never achieved even at the end of the heat treatment; we argue that the two grain families keep a different ordering with the fine grains characterized by a higher disorder and, thus, higher B_{c2} values.

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